

# $E \otimes e$ Jahn-Teller Effect in $C_{70}^{3-}$ Systems

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## Abstract

The electron-phonon interaction in  $C_{70}$  anions is studied by making use of a lattice relaxation approach. We find there exists a Jahn-Teller effect in  $C_{70}^{3-}$  system, due to an extra electron being doped to the double degenerate  $E_1''$  state. As a result of this effect, the original  $D_{5h}$  symmetry of the ground state becomes unstable, which causes distortion of the lattice configuration. The only symmetry maintained in the final state of the relaxation is the  $x$ - $y$  plane reflection symmetry. We further find that besides the Jahn-Teller active  $A_1'$ ,  $A_2'$ ,  $E_2'$  modes, the non-Jahn-Teller active  $E_1'$  vibrations also contribute to the relaxation process, which come from the nonlinear effect and are two or three orders smaller than those of the Jahn-Teller active modes. We suggest that the  $C_{70}^{3-}$  molecule is a promising Berry Phase candidate in this effective  $E \otimes e$  Jahn-Teller system.

In many physics systems, such as the low dimensional crystals and clusters, both the electronic structure and the vibronic structure are affected by the electron-phonon coupling. The  $C_{70}$  molecule, with its  $D_{5h}$  symmetry that includes double degenerate and nondegenerate irreducible representations, is a perfect system to study the electron-phonon interaction in the electron-lattice systems. Since the discovery of  $C_{70}$  about ten years ago [1], there are massive experiments exploring various properties of  $C_{70}$ , such as Raman spectra [2,3], photon luminescent and absorption spectra [4–6], *et al.* Many properties of the geometry and electronic structure of  $C_{70}$  have also been calculated by using different methods such as quantum chemical calculation [7], first principle LDA [8,9], vibrational potential method [10], mean field method [11] and *ab initio* Hartree-Fock method [12,13]. But none of the above methods can obtain both the vibronic property and the electronic property self-consistently, and all of them need huge computation.

In this paper, we study the electron-phonon coupling in  $C_{70}$  anions by using the simple and elegant Su-Schrieffer-Heeger (SSH) model. It is well known that the ground state of neutral  $C_{70}$  molecule has  $D_{5h}$  symmetry which is composed of 20 group elements including pentagon rotation and  $x$ - $y$  plane reflection. The  $D_{5h}$  group has 8 unequivalent irreducible representations (IR),  $A'_1$ ,  $A'_2$ ,  $A''_1$ ,  $A''_2$ ,  $E'_1$ ,  $E'_2$ ,  $E''_1$  and  $E''_2$ . Both the electron levels and the phonon levels of  $C_{70}$  can be classified by these 8 IRs that are either single or two fold degenerate. Generally, when the electron filling in molecules changes, the effective potential, which includes both the elastic energy between the lattice atoms and the electron-lattice coupling energy, is subject to modify accordingly. On the new potential surface, the effective potential of the original lattice configuration deviates from the minimum points and the system becomes unstable, that will result in a lattice relaxation process until a new stable point finally being reached. During this process, the lattice symmetry may be broken depending on electronic doping. If an additional electron is doped to a nondegenerate level, only the total symmetric modes participate in the lattice relaxation according to the Jahn-Teller theorem. The original symmetry of the lattice will not be broken by these modes and the degenerate electron levels will not split. However, when the electron is filled to a

degenerate level, the Jahn-Teller active modes will include non-total symmetric vibrations besides the total symmetric modes. Lattice displacements along the directions of these non-total symmetric modes will reduce both the lattice symmetry and the degeneracy of the electron levels. In neutral  $C_{70}$ , the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are both nondegenerate, with  $A_2''$  and  $A_1''$  symmetry respectively, while the next higher level (the 37th, 38th level) above the Fermi surface is double degenerate. The salient difference between  $C_{70}^-$  or  $C_{70}^{2-}$  (lighter doping) and  $C_{70}^{3-}$  (heavier doping) is that the former case only involves electronic filling in a non degenerate level whereas the latter involves in a degenerate one. In the cases of  $C_{70}^-$  and  $C_{70}^{2-}$  clusters where the extra electrons are doped to the  $A_1''$  LUMO level, the  $D_{5h}$  symmetry is maintained in the final state, since the lattice displacement from the original configuration contains only  $A_1'$  vibration modes which are totally symmetric. In the case of  $C_{70}^{3-}$ , the third electron is filled to the next higher level ( $E_1''$  representation), after the LUMO is fully occupied by the other two extra electrons. The Jahn-Teller active modes in this case include  $A_1'$ ,  $A_2'$  and  $E_2'$  vibrations. As a result, the original  $D_{5h}$  symmetry is broken after relaxation and all the electron levels become nondegenerate. From further analysis (see below), we find that all the participating modes in this process will maintain the  $x$ - $y$  plane reflection symmetry, which is the only symmetry left after the lattice relaxation. It is worth to point out that other non-Jahn-Teller modes besides the Jahn-Teller active modes may also make contribution once the lattice relaxation evolves. This is due to the non-linear effect, which is involved in coupling between the vibration modes in the effective potential. The nonzero contribution of the non-Jahn-Teller active modes is proportional to the displacement of the Jahn-Teller active mode, so that the displacements along these non-Jahn-Teller active modes may be substantially smaller than that of the Jahn-Teller active modes. We find that in  $C_{70}^{3-}$  anion there only exists one kind of non-Jahn-Teller active modes,  $E_1'$  modes, whose amplitudes are two or three orders smaller than that of the  $A_1'$ ,  $A_2'$ , and  $E_2'$  vibrations. From the above analysis, it is clear that the  $C_{70}^{3-}$  system reduces to an effective  $E \otimes e$  Jahn-Teller model [14,15] which carries the Berry Phase, where  $E$  and  $e$  are the group representations of

the electron and vibration modes respectively. We suggest that the  $C_{70}^{3-}$  system is a promising candidate to verify the Berry Phase and the corresponding selection rules featured by the  $E \otimes e$  Jahn-Teller model. As it is relatively easy to charge  $C_{70}$  in laboratories, our results may be observed and verified by further experiments.

The SSH model has the following form [16]:

$$\begin{aligned}
H = & - \sum_{\langle i,j \rangle, s} (t_0 - \alpha(l_{ij} - l_1))(c_{is}^\dagger c_{js} + h.c) \\
& + \frac{1}{2} K_1 \sum_{\langle i,j \rangle} (l_{ij} - l_1)^2 \\
& + \frac{1}{2} K_2 \sum_{i'} d\theta_{i,5}^2 + \frac{1}{2} K_3 \sum_{i'} (d\theta_{i,6,1}^2 + d\theta_{i,6,2}^2) \\
& + \frac{1}{2} K_4 \sum_{i''} d\theta_{i,6,3}^2 + \frac{1}{2} K_5 \sum_{i''} (d\theta_{i,6,1}^2 + d\theta_{i,6,1}^2)
\end{aligned} \tag{1}$$

where  $t_0$  is the hopping integral between nearest neighbour carbon atoms;  $\alpha$  is the e-ph coupling constant; and  $l_{ij}$  is the bond length between different atoms with  $l_1$  being the bond length with all the bond stretching springs relaxing.  $c_{is}^\dagger$  ( $c_{is}$ ) are the electron creation (annihilation) operators of the  $\pi$  electron on site  $i$  with spin index  $s$ .  $d\theta_{i,5}$ ,  $d\theta_{i,6,1}$ ,  $d\theta_{i,6,2}$ ,  $d\theta_{i,6,3}$  are bond angle deviations from the original angle,  $108^\circ, 120^\circ, 120^\circ, 120^\circ$  respectively, *e. g.*  $d\theta_{i,5} = \theta_{i,5} - 108^\circ$ , *etc.*  $K_i$  ( $i = 1$  to  $5$ ) are the elastic constants for different kinds of lattice vibrations. The primes above the summation in the  $K_2$  and  $K_3$  terms indicate exclusion of the middle ten atoms near the equator, while the double primes in the  $K_4$  and  $K_5$  terms denote that the summation includes only the equatorial ten atoms because the geometry condition for them are different from the others. The first term in this formula is the tight binding electron Hamiltonian describing  $\pi$  electrons hopping between the nearest neighbour sites. The  $K_i$  terms are the elastic energies of the lattice atoms in the form of classical springs. The kinetic energies of atoms are not included in the Hamiltonian in the adiabatic approximation. The springs of the angular terms are introduced to represent the degrees of freedom that can not be represented by pure bond-length terms. The  $\alpha$  term inside the tight-binding electron Hamiltonian represents the linear electron-phonon interaction which is valid when the lattice displacements are small. We use the following set

of parameters:  $\alpha = 6.20 \text{ eV/\AA}$ ,  $t_0 = 2.50 \text{ eV}$ ,  $K_1 = 42 \text{ eV/\AA}^2$ ,  $K_2 = 8.0 \text{ eV/rad}^2$ ,  $K_3 = 7.0 \text{ eV/rad}^2$ ,  $K_4 = 6.5 \text{ eV/rad}^2$ ,  $K_5 = 6.0 \text{ eV/rad}^2$ . Our results fit well with experimental observable data which show that these parameters are reasonable. The coulomb interaction is not considered in this model as the electron-electron interaction contributes little to the lattice relaxation. This conclusion is came from another work [17], where the coulomb interaction is analysed and shows no important effects on the Jahn-Teller system. We solve this model in a framework of the Bogoliubov-De Gennes(BdG) formalism and get the stable point in the adiabatic potential surface self-consistently. Both the lattice configuration and the electron state are derived within simple calculation. The advantage of this model is that we can get the electronic and the vibronic properties together. Comparing it with more complex and sophisticated methods, such as LDA, the SSH model only has a few parameters but grasps the essential physics. Our calculations show that it is a suitable model to deal with the fullerene family.

We apply the dynamical method [16] to approach the stable point gradually on the effective potential surface. Starting from an initial configuration, we calculate the electron levels and the effective potential  $V_{\text{eff}}$ , derive the force on each atom from the  $V_{\text{eff}}$  that is exerted by both the electrons and other atoms, and get lattice displacements that are caused by these forces, then start a new round by using new configuration. This dynamic process is repeated until the stable point (the minimum) on the potential surface being reached. The following equations are necessary:

$$\begin{aligned} F_{i\sigma} &= -\frac{dV_{\text{eff}}}{dx_{i\sigma}} \\ v_{i\sigma} &= \frac{dx_{i\sigma}}{dt} \end{aligned} \tag{2}$$

where  $V_{\text{eff}}$  is the effective lattice potential that includes the elastic energy between the lattice atoms and the electron-lattice interaction energy that also is function of the lattice coordinates.  $F_{i\sigma}$  is a force component in direction  $\sigma$  on atom  $i$  that is derived from the effective lattice potential.

We can also derive the phonon modes by this simple model. Making use of the final configuration of the relaxation, we can derive the vibration frequencies and vectors by adding the kinetic parts to the lattice Hamiltonian and applying the elastic coefficient matrix method. The following equations are used:

$$\begin{aligned}
H_{\text{eff}} &= \frac{1}{2}m \sum_{i,s} \left(\frac{dx_{i,s}}{dt}\right)^2 + \frac{1}{2}K_{i,s;j,s'}x_{i,s}x_{j,s'} \\
K_{i,s;j,s'} &= \frac{\partial^2 V_{\text{eff}}}{\partial x_{i,s} \partial x_{j,s'}} \\
V_{\text{eff}} &= V_{\text{elas}} + V_{e-ph}
\end{aligned} \tag{3}$$

where  $x_{i,s}$  is a small displacement of atom  $i$  from its equilibrium position in the  $s$  direction,  $K_{i,s;j,s'}$  is an element of the elastic coefficient matrix. The first term of the Hamiltonian is the kinetic energy of the lattice atoms and the second term is the effective potential energy related to the equilibrium position of the lattice.  $V_{\text{eff}}$  is composed of two parts: the elastic energy of the lattice  $V_{\text{elas}}$  and the e-ph coupling energy  $V_{e-ph}$ , that is derived by the second order perturbation [16] from the e-ph coupling Hamiltonian and by omission of the higher order parts. Using Eq. (3), we get the elastic coefficient matrix and find the eigenvalues and eigenvectors, which are just the phonon modes. The group representation of these vibration modes can be determined by the projection method that uses characters of  $D_{5h}$  group elements.

The first results we get are the lattice structures of the neutral  $C_{70}$  and  $C_{70}^-$  anions, all of that have the shape of prolate. We list the bond lengths and angles of these clusters in Table (1). Having  $D_{5h}$  symmetry in  $C_{70}$ ,  $C_{70}^-$ , and  $C_{70}^{2-}$ , there are 3 kinds of bond lengths in these clusters. The short bond length is 1.35 Å besides these two kinds of bond there is another type of bond whose length is about 1.42 Å, and its value is between the long and short bond. The middle length bonds have the same character as the bond in the Graphite. The main difference among these  $C_{70}$  clusters is that the doped clusters have longer bond length in the neighbourhood of the equator, whose structure is looser than the neutral one. The electron density near the equator plane is larger, hence the

electron screening of the lattice elastic interaction is stronger. This phenomena can explain the bond length's difference. As a result, the skeleton of the  $C_{70}^{2-}$  is looser than that of the  $C_{70}^-$  molecule. It seems that the central ten atoms are inserted equatorially in the  $C_{60}$  ball like a loose chain without dimerization. This point can also be seen in the bond angles which are almost the same as that of  $C_{60}$  for all atoms except the equatorial ones, that have the largest deviation of  $2.0^\circ$  from  $120^\circ$  in the hexagon. The small deviation of the angles shows that the elongation of the  $C_{70}$  molecule from the ball shape is very small. In  $C_{70}^{3-}$ , the pentagon symmetry  $C_5$  is broken, and the bond angles and bond lengths in the same layer of the prolate are not the same, but the overall structure is also a prolate with very small deviation.

In neutral  $C_{70}$ , as the lattice symmetry of  $D_{5h}$  is relatively lower than the  $I_h$  symmetry of  $C_{60}$ , there are only double degenerate and non-degenerate electron levels which locate close to each other. The electrons fill in the lower 35 levels and all the anti-bond states are empty. The total symmetry of this many electron state is  $A_1'$ . The gap between HOMO and LUMO is 2.14 eV, which agrees well with the experimental result [4]. This certifies that the set of parameters we choose is reasonable since the gap value varies sensitively with the parameters used in the calculation. The group representations of HOMO and LUMO are  $A_2''$  and  $A_1''$  respectively, both of them being non-degenerate states. Hence, if extra electrons are charged to the LUMO, which is non degenerate, which is the case of  $C_{70}^-$  or  $C_{70}^{2-}$ , the  $D_{5h}$  symmetry will not be lowered and the Jahn-Teller effect will not occur. Another such example is the lowest energy exciton with one electron being excited from the HOMO to the LUMO. This exciton is an  $A_2'$  state which also is non-degenerate [17]. In these cases, the lattice displacement between the final state and the initial state before relaxation contains only the total symmetric  $A_1'$  vibrations which will keep the  $D_{5h}$  symmetry, as is listed in Table (3.a). But this is not the case in the  $C_{70}^{3-}$ , as will be discussed in detail later. The total energy in the new configuration is lower than that of the initial one, hence the new state is more stable. In  $C_{70}^-$ , the gap drops to 1.91 eV after the lattice relaxation; in  $C_{70}^{2-}$ , when the LUMO is filled up, the gap drops further to 1.69 eV in the stable state, that

indicates the gap is reduced upon doping. From the energy spectrum, we find that the LUMO drops greatly, and the HOMO level and all the other states almost do not change upon doping. This is the polaron effect which results from the electron-phonon coupling. The electron wavefunction is localized near the plane next to the equator as it has been shown by the electron density on atoms.

In an electron-lattice interaction system, the electron filling can affect the atomic configuration, and in return, the lattice configuration will determine the electron wavefunctions and levels also. The difference between the electron densities in various electron fillings manifests this mutual interaction. When the electron density in a site is denser, the electron-lattice interaction will screen more of the elastic force acting on the nearby atoms. Then, the bond length related to the atoms will become more relaxed and becomes longer. In Table (2), our results for the electron densities in five kinds of points (which were certified by the NMR experiments [1]) in different kinds of clusters are listed. The density differences between different points are small since  $C_{70}$  is approximately spherical with the height along the pentagon axis being a little longer than the diameter of the equator plane. In the doped clusters, the electron densities on atoms near the equatorial plane and around the two tops do not change much from that of the neutral cluster. The additional electron density due to doping distributes mainly on the plane that is next to the equator. It agrees with the bond length distribution. Upon doping,  $a_6$  and  $a_4$  become longer due to the screening of the elastic interaction.

In  $C_{70}^{3-}$  anion, when the third extra electron is doped to the level immediately higher than LUMO, which is a double degenerate  $E_1''$  level, the  $D_{5h}$  symmetry of the initial lattice configuration is destroyed during relaxation, and all the electron levels become non-degenerate, due to the static Jahn-Teller effect. The motion of the lattice coordinate can be discussed on the effective potential surface in the configuration space. When the electron filling changes, the lattice configuration jumps from the initial potential surface to another surface on which the lattice configuration is not at the minimum point of the potential. Then, the initial configuration becomes unstable and the cluster begins the lattice relaxation process. At



the point when the relaxation just starts, the vibration modes that couples to the lattice motion include only the Jahn-Teller active modes. At this point, the derivatives of effective potential in the Jahn-Teller active vibration directions are not zero, while the derivatives along all other directions are zero.

Phonon modes are Jahn-Teller active when they satisfy the following equation:

$$\langle e | \frac{\partial H}{\partial Q_\nu} | e \rangle \neq 0 \quad (4)$$

where  $Q_\nu$  is the displacement along phonon mode  $\nu$ , and  $|e\rangle$  is the electron state that depends on the lattice displacement. Using symbols of group theory, Eq.(4) can be interpreted as follows:

$$G^e \otimes \overline{G^e} \otimes \overline{G^{ph}} \supset A'_1 \quad (5)$$

where  $G^e$  is the group representation of multielectron state with  $\overline{G^e}$  being its complex conjugate counterpart. Here,  $G^e = \overline{G^e}$  since the representation is real.  $\overline{G^{ph}}$  is the complex conjugate representation of phonon mode. In the  $C_{70}^{3-}$ , the above equation is equivalent to:

$$E''_1 \otimes E''_1 \supset A'_1 \oplus A'_2 \oplus E'_2 \quad (6)$$

From this equation, not only the total symmetry  $A'_1$  vibrations contribute to the dynamical process in the beginning, but  $E'_2$  and  $A'_2$  modes may also participate in the process. These three kinds of modes are the Jahn-Teller active modes that will break the lattice symmetry. From the first step on, the lattice will reach to the new minimum point on the new potential surface after a relaxation period. All the participating modes have  $x$ - $y$  plane reflection symmetry. So, only the  $x$ - $y$  plane reflection symmetry is left unperturbed while the pentagon rotation symmetry is broken, and the degenerate electron levels split into single levels.

All the above analytical results can be checked numerically by using the dynamical method. Within the simple SSH model, we can get all the quantities, the lattice configuration of the neutral  $C_{70}$  and the  $C_{70}^{3-}$ , and the phonon canonical vectors. The lattice displacement during the relaxation process is just the difference between the lattice coordinates of the

initial and the final state. We project this displacement to the normal vector of the phonon modes to get amplitude  $Q_\nu$  in  $\nu$  direction. Let  $x_{i,\sigma}^{(0)}$  be the lattice position of the neutral cluster, and  $x_{i,\sigma}^{(3)}$  be the lattice position of the  $C_{70}^{3-}$  anion, then,

$$Q^\nu = \sum_{i,\sigma} (x_{i\sigma}^{(3)} - x_{i\sigma}^{(0)}) \xi_{i,\sigma}^\nu \quad (7)$$

where  $\xi_{i,\sigma}^\nu$  is the phonon vibration vector. Using this method, we derive the contributions from different phonon modes. In our numerical results, the modes that give non-zero contributions are  $A'_1$ ,  $E'_2$ , and  $E'_1$  among which  $A'_1$  and  $E'_2$  are Jahn-Teller active modes. All the amplitudes in  $E'_1$  are two or three orders smaller than those of the  $A'_1$  and  $E'_2$  modes. The absence of the Jahn-Teller  $A'_2$  modes does not contradict with the Jahn-Teller theorem. After the first step in the relaxation process, the symmetry of the cluster is decreased, other phonon modes may join the process too. This can be explained by the effective potential approach. We can write the effective potential in Taylor expansion and select the initial position as the zero point. The initial force on the lattice atoms can be projected only to the Jahn-Teller direction. The force at the zero point only results from the first order terms of the effective potential since all the higher order terms at this point are zero. But, if the displacement from the initial point is not zero, the higher order terms may also make contribution. There are coupled terms between different lattice vibrations, hence, non-Jahn-Teller modes may participate the relaxation. Since the forces from the second order terms are proportional to the lattice displacement, it will be several orders smaller because the lattice distortion is not large. In  $C_{70}^{3-}$ , we can find that the modes that couple to the Jahn-Teller modes in the second order terms of the effective potential are only the  $E'_1$  modes. Our calculation certifies this point. And the  $E'_1$  displacements are reasonably small. In Table (3.b), we list the amplitudes of those modes that give non-zero contributions as well as the frequency of those modes. The unit of the frequency is  $cm^{-1}$ . In table (3.a), we also list lattice displacements of the  $C_{70}^-$ ,  $C_{70}^{2-}$  and  $C_{70}$  exciton, which are nonzero only in the  $A'_1$  directions, since the corresponding single electron states are nondegenerate.

Since the third doping-electron in  $E''_1$  state couples strongly to  $E'_2$  state, it turns out

the  $C_{70}^{3-}$  system can be represented by an effective  $E \otimes e$  Jahn-Teller model that has been thoroughly studied for several decades [14,15]. It is well proved that there exists Berry Phase in the  $E \otimes e$  effective system. The consequent selection rules found in this system are intriguing and have been observed by many experiments [15]. Hence we may further suggest the possibility of the presence of the Berry Phase, *i. e.*, the sign change in the electronic wave functions under a  $2\pi$  rotation in the space of the vibrational coordinates, in  $C_{70}^{3-}$  system which might be the first polymer sample to manifest the fascinating  $E \otimes e$  model. We wish our prediction can be observed experimentally within the reach of the current technology.

In conclusion, we have carefully studied the electron-phonon interaction in the  $C_{70}$  molecule. In particular, the static Jahn-teller effect in the  $C_{70}^{3-}$  is discussed. The lattice displacement from the neutral  $C_{70}$  to the  $C_{70}^{3-}$  anion is projected to the canonical vibration vector space.. The nonzero contributions among these projections are the Jahn-Teller active  $A'_1$  and  $E'_2$  modes, as well as the non-Jahn-Teller active  $E'_1$  modes that couple to the Jahn-Teller active modes through the second order non-linear terms in the effective potential. The contributions of  $E'_1$  modes are comparably smaller than those of the Jahn-teller active modes since the former depends on the lattice distortions that are very small. We find that  $C_{70}^{3-}$  is an effective  $E \otimes e$  e-ph system, and the Berry Phase might be presented in such a system. Our results show that the SSH model is a convenient and self-consistent model to study the electron-lattice interaction in the fullerene family.

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**Table 1 (a)** Listed below are bond lengths of  $C_{70}$  and its anions. The results of  $C_{70}^{3-}$  are not listed due to the broken symmetry.

	f	2	3	4	5	6	7	8
$C_{70}$	f thf447	felectron dea97	f thf446	f thfa(e3	f.453	f thf421	f.418	f.448
$C_{70}^-$	f thf448	fea(e8	f thf446	f.403	f.441	fe431	f thf420	f.445
$C_{70}^{2-}$	f thf448	f.a(e8	f.446	fe413	fe429	f.443	f.420	f.443

**Table 1 (b)** The calculated bond angles from a through l of  $C_{70}$  and  $C_{70}^\pm$  together with experimental results are listed. The † has the same meaning as that in table(1).

	a	b	c	d	e	f	g	h	i	j	k	l
$C_{70}$	f08.0	f19.9	f20.0	f07.7	f20.1	f07.9	120.1	f20.3	f19.1	f08.3	118.0	f19.6
$C_{70}^-$	f08.0	f20.0	f20.0	f07.6	119.9	108.0	120.0	120.5	f19.0	108.2	f18.1	119.5
$C_{70}^{2-}$	108.0	120.1	f20.0	107.7	f19.8	f08.0	f20.0	f20.5	f19.0	f08.2	f18.1	119.5

**Table 2** Electronic densities on 5 kinds of positions from A to E of  $C_{70}$  and  $C_{70}^\pm$  are shown. The † has the same meaning as that in table(1).

	A	B	C	D	E
$C_{70}$	0.991	f.013	0.996	f.012	0.980
$C_{70}^-$	0.988	f.015	f.021	f.038	0.980
$C_{70}^{2-}$	0.986	f thf016	f.046	f.064	0.979

**Table 3 (a)** Lattice relaxations between ground state and the lowest exciton state,  $C_{70}$  anions are projected to different phonon modes. The results listed in this table are projections to  $A_1'$  modes. The contribution of all other modes are zero.

	f3	23	38	53	59	93	125	138	142	154	178	210
$C_{70}^-$	-0.058	0.020	-0.008	0.002	0.008	0.014	-0.022	0.020	0.009	0.004	0.006	0.014
$C_{70}^{2-}$	-0.159	0.048	-0.017	0.005	0.017	0.028	-0.044	0.040	0.017	0.008	0.012	0.028
Exciton	-0.138	0.035	-0.022	0.015	0.015	0.026	-0.041	0.036	-0.002	-0.002	0.009	0.025

**Table 3 (b)** Lattice relaxations between ground state and the lowest exciton state,  $C_{70}^{3-}$  are projected to different phonon modes.

$A'_1$ (/cm)		$E'_2$ (/cm)			$E'_1$ (/cm)		
229	-0.178	187	-0.040	-0.021	240	$-1.5*10^{-4}$	$-1.2*10^{-4}$
302	0.050	219	0.010	-0.018	275	$-1.1*10^{-5}$	$-7.5*10^{-8}$
380	-0.007	317	-0.016	-0.009	315	$-f\ thf1*10^{-4}$	$f\ thf6*10^{-4}$
452	0.012	371	-0.002	0.004	347	$-2.0*10^{-5}$	$2.9*10^{-5}$
479	0.019	413	-0.001	$6.2*10^{-4}$	422	$-f\ thf1*10^{-4}$	$-9.9*10^{-5}$
687	0.031	477	-0.005	0.002	4a(e	$-3.4*10^{-5}$	$2.9*10^{-5}$
f050	-0.042	494	-0.003	-0.006	524	$3.5*10^{-5}$	$-3.1*10^{-5}$
1232	0.043	555	-0.003	0.006	538	$-4.0*10^{-5}$	$-5.5*10^{-5}$
1299	0.033	611	-0.002	0.003	565	$-f\ thf9*10^{-5}$	$-1.7*10^{-5}$
1357	0.022	711	0.007	-0.004	686	$5electron\ dea*10^{-5}$	$7.0*10^{-5}$
1512	0.009	736	-0.006	-0.004	875	$-5e3*10^{-5}$	$-6.4*10^{-5}$
1724	0.030	846	$4.6*10^{-4}$	$2.5*10^{-4}$	933	$-5e6*10^{-5}$	$-6.9*10^{-5}$
		9a(e	0.007	-0.004	f111	$f.4*10^{-4}$	$f.0*10^{-4}$
		f024	-0.002	0.001	f202	$9.2*10^{-5}$	$-1.1*10^{-4}$
		1235	0.001	-0.001	f340	$-8.8*10^{-5}$	$-f\ thf1*10^{-4}$
		1325	0.003	-0.003	1371	$f.1*10^{-4}$	$-8.4*10^{-5}$
		1377	-0.004	0.003	1419	$-6.7*10^{-5}$	$8.7*10^{-5}$
		1593	$6.0*10^{-4}$	0.002	f477	$-4.3*10^{-5}$	$2.6*10^{-5}$
		1623	-0.005	0.003	1504	$2.1*10^{-5}$	$2.6*10^{-5}$
		1708	$-5e0*10^{-4}$	0.030	1605	$3.0*10^{-5}$	$-3.9*10^{-5}$
		1738	0.010	0.008	1680	$1.1*10^{-5}$	$-5.0*10^{-4}$
					f728	$-2.4*10^{-5}$	$f\ thf5*10^{-5}$